Graphene on metal surface: gap opening and n-doping

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Graphene grown on metal surface, Cu(111), with a boron nitride(BN) buffer layer is studied for the first time. Our first-principles calculations reveal that charge is transferred from the copper substrate to graphene through the BN buffer layer which results in a n-doped graphene in the absence of a gate voltage. More importantly, a gap of 0.2 eV which is comparable to that of a typical narrow gap semicondutor opens just 0.5 eV below the Fermi-level at the Dirac point. The Fermi-level can be easily shifted inside this gap to make graphene a semiconductor which is crucial for graphene-based electronic devices. A graphene based p-n junction can be realized with graphene eptaxially grown on metal surface.

PACS numbers:

Graphene, first isolated by Novoselov[1], have attracted a lot of research interest recently because of its intriguing physics for fundamental studies and its potential applications for the next generation electronic devices, such as novel sensors[2] and post-silicon electronics.[3,4,5,6] As a 2D crystal, graphene was found not only to be continuous but to exhibit high crystal quality,[1,7,8] in which charge carriers can travel thousands of interatomic distances without being scattered.[9,10,11] In addition, due to its special honeycomb structure, band structure of graphene exhibits two intersecting bands at two inequivalent K points in the reciprocal space and its low energy excitations are mass-less Dirac fermions near these K points because of its linear (photon-like) energy-momentum dispersion relationship. This results in very high electron mobility in graphene which can be further improved significantly, even up to $\approx 10^5$ cm^2/V·s. It also allows controls of carrier type (electron-like or hole-like) and density by electric-field[1]. These are different from conventional doping of semiconductors, for example via ion implantation. With such features, graphene is promising in many applications, such as bipolar devices which comprises junctions between hole-like and electron-like regions, and p-n junctions which can be configured by gate-voltage within a single atomic layer.[12,13,14] Graphene based devices can be expected to have much more advantages than silicon-based devices.

At present, there are mainly two methods of producing graphene samples. In the first, an almost freestanding graphene is produced by mechanically splitting off bulk graphite crystals and depositing it onto a SiO$_2$/Si substrate.[15] Although this method is very convenient, it is difficult to produce high quality graphene structures. In the second method, an ultrathin graphene layer is formed by vacuum graphitization through silicon deple-

tion from a SiC surface.[16] The large lattice mismatch between SiC substrate and graphene results in graphene produced using this method being fragile and containing many defects.[17] It is thus desirable to find a way of fabricating graphene which can overcome the above disadvantages. Pristine graphene is a zero-gap semiconductor because its Fermi level exactly crosses the Dirac point. An energy gap is required for many practical applications.

A gap can be induced in graphene by a weak interaction with the substrate when it is grown on a suitable substrate.[18] However, choosing the right substrate is not trivial. If the interaction is strong, the advantages of graphene will be lost which is the case when a single layer of graphene grown on SiC.[19] On the other hand, a too weak interaction between graphene and the substrate is not able to change the property of graphene and to open a gap.[20] Attempts were made to grow graphene directly on metal substrate,[21,22] which provides an interaction stronger than van der Waals interaction (such as graphene grown on h-BN substrate[20]) but weaker than covalent interaction (such as that between graphene and a SiC substrate[19]), which indeed led to opening of band gap. In addition, large area of flat single-crystal metal surface is easy to obtain experimentally. Therefore, metal substrate can be useful in graphene-based electronic-devices. The only drawback is that the energy bands and the Dirac cone of graphene are submerged in the electronic sea of metal and the unique property of graphene cannot be utilized when it is grown directly on metal substrate. It is thus important to find proper substrate to overcome this disadvantage. In this work, we investigate graphene grown on Cu(111) substrate with a boron nitride (BN) buffer layer between them. The experimental lattice constant of Cu(111) surface is 2.55 Å which is very close to those of the BN sheet (2.50 Å) and graphene (2.46Å). The slight mismatch is acceptable since the C-C bond and B-N bond are very strong. It is noted that in the growth of graphene directly on SiC, the excess carbon atoms self-organize to form the honeycomb structure

which overwhelms the covalent bonding with substrate, even through the lattice mismatch between the graphene layer and the SiC substrate is as high as 8%.[17] Thin carbon layer consisting of sp^2-hybridized carbon modification in the form of graphene stacks over copper nanoparticles have been produced.[23] Heteroepitaxial graphene/h-BN double layer has also been realized on some metal substrate by chemical vapor deposition(CVD).[24] It can be expected that including a BN buffer layer will improve the stability of the heteroepitaxial graphene/h-BN structure on Cu(111) surface. Furthermore, the special electronic structure of this system ensures that it will be more suitable for applications in electronic devices, which will be further discussed below.

First-principles calculations based on the density functional theory were performed using the VASP code[25,26,27,28] The projector augmented wave pseudopotentials[29]were used for electron-ion interactions while the local density approximation (LDA) was used for exchange-correlation function. A special $36\times36\times1$ k-point sampling was used for the surface Brillouin-zone integration. The plane wave basis set was restricted by a cutoff energy of 400 eV. The in-plane lattice constant of the heteroepitaxial graphene/h-BN/Cu(111) structure was set to 2.49 Å which is the lattice parameter of Cu(111) determined from our first-principles calculation within LDA. In structural relaxation, five atomic layers of Cu were used to model the substrate, with atoms in the bottom two layers fixed to their bulk positions and h-BN and graphene adsorbed to the top surface. Electronic structure calculations were carried out using a ten layer substrate model with two center layers fixed. Graphene and BN layer are adsorbed on both sides. A vacuum region of at least 18 Å was used to avoid interaction between the top and bottom surfaces. All structures were fully relaxed, and the forces acting on an atom is ≤ 0.03 eV/Å in the relaxed structures.

The graphene and BN layers were placed on the 1×1 unit cell of Cu(111). There can be different atomic arrangements for BN and graphene relative to the substrate. First of all, the BN sheet can have six different arrangements over Cu(111), with either B or N on the fcc or hcp site, and atop a Cu atom of the substrate, respectively. Among these, two arrangements, with N on the atop site while B on either the fcc or hcp site as shown in Fig. 1(a) and Fig. 1(b), respectively (referred as structures A1 and A2 respectively in the following), are energetically favored. They are very similar to the structure of BN sheet on Ni(111).[24] The energies of these two structures are almost the same and are lower than those of other structures by more than 20 meV. The distance between the BN sheet and the Cu(111) surface is about 2.70 Å for the A1 arrangement and 2.79 Å for the A2 arrangement, which is smaller than the distance between adjacent atomic layers in bulk h-BN (3.35 Å) but larger than that between a BN sheet and the Ni(111) surface.[24] Therefore, the strength of interaction between the BN sheet and Cu(111) can e expected to be stronger than

that between the BN layers and weaker than that with the Ni(111) substrate. In the relaxed structure, the B and N atom are found not in the same plane, and the N atom which is at the atop Cu site is a slighly higher (~ 0.02 Å) than B atom which is located at the hollow site. This rumpling is also much smaller compared to that of BN on Ni(111) substrate where a rumpling of 0.18 Å was observed experimentally. This is also an indication of relatively weaker interaction between the BN layer and Cu(111) substrate, compare to Ni(111).

To find the most stable structure of graphene on BN/Cu(111), self-consistent calculations were performed for all possible geometries between the graphene and the above two most stable BN arrangements on Cu(111). Relative to the BN lattice, carbon atoms of the graphene can be directly over the B and N atoms, or one carbon atom in the hollow site and the other above either a B or a N atom. Among the six possible heteroepitaxial structures, the two atomic arrangements A1 (Fig.1a) and A2 (Fig.1b) are energetically degenerate and are predicted to be most stable. In both structures, one graphene sub-lattice is over the B atom. The other sub-lattice is on the hcp hollow site of Cu(111) in A1 while it is on the fcc hollow site of Cu(111) in A2. The graphene floats over the BN sheet at a height of ~ 3.0 Å, slightly smaller than inter-layer distance of graphite. This confirms that LDA, despite the lack of long-range nonlocal correlations, produces reasonable interlayer distances in layered van der Waals crystal, such as graphite and h-BN, for a delicate error cancelation between exchange and correlation which underlies this apparent performance of LDA.[30] The distance between BN sheet and Cu(111) changed by -0.3 Å after adsorption of graphene. However, the distance between Cu layers remains essentially the same as that in a clean Cu(111) surface. Further structural details are given in Table I.

Figs. 2(b) and 2(c) show the band structure of optimized atomic arrangement A2 before and after graphene adsorption, respectively. For reference, the band structure of clean Cu(111) surface is shown in Fig. 2(a). The d-bands of copper are apparent in all three band structures and are essentially unaffected by BN and graphene due to the weak interaction with them, except at the Γ point near the Fermi level. After adsorption of the BN sheet, bands characteristic of h-BN appear at about -18 eV in the band structure while the occupied p-bands of BN appear at about 4 eV below the Fermi level at the Γ point. The most interesting feature is the appearance of a band in the energy gap of Cu(111) at K about 2 eV above the Fermi level. In perfect BN sheet, this valence band minimum is about 18.4 eV above the lowest s-band at K within LDA calculation, but it is reduced to about 18.2 eV after the BN sheet is adsorbed on Cu(111). This shift is due to surface dipole effect of Cu(111) substrate, as indicated by the change of work function of the Cu(111) surface from 5.25 eV to 4.83 eV after BN adsorption. Electrons redistribe in response to the dipole effect, resulting also to the slight downward

shift of some Cu(111) bands at M and the upward shift of some bands at Γ around the Fermi level. Nevertheless, the BN layer remain insulating since the Fermi level does not cross any BN bands. After graphene adsorption, the Cu(111) bands at Γ become completely unoccupied and bands characteristic of graphene appear in the energy range of −18 eV to −4 eV. The Dirac cone at K is located in the energy gap of the substrate, just 0.5 eV below the Fermi level. The linear relationship between energy and momentum is maintained. This indicates that the graphene is n-doped with excess carriers induced by the substrate. In addition, a band gap of about 0.2 eV opens at K for graphene which is much larger than that of graphene on h-BN substrate[20], although the interfacial atomic arrangement between graphene and h-BN is the same in both cases. As mentioned above and shown in Fig.1(b), one sublattice of graphene is located directly above B or the hcp hollow site of Cu(111) while the other is at the hexagonal center of h-BN honeycomb or the fcc hollow site of Cu(111). Interaction between the Cu(111) substrate and BN leads to redistribution of charge of BN sheet since the BN plane is a little rumpled. Thus the gap opening of graphene can be understood based on the symmetry breaking the A and B sublattice equivalence, which leads to the rehybridization of the valence and conduction band states associated with the same Dirac point (see Fig.3(b) and Fig.3(c)). This gap is essential for graphene-based electronic devices for controlling conductivity.

Although the Dirac point of graphene is located in the energy gap of the Cu(111) substrate at point K of reciprocal space, the electronic structure of the graphene layer at the other points of momentum space is unknown, which would have influence on conductivity. The K-resolved DOS, which is equivalent to ARUPS experiment, of the graphene layer of the A2 structure is shown in Fig.3(a). The band structure is almost the same as that of perfect graphene except the position of the Fermi-level (The energy gap cannot be seen clearly at K which is due to the resolution in the calculated DOS). No other states were observable in this graphene layer. Therefore, the electronic property of the graphene layer shows features of a typical n-doped graphene. However, it is noted that this occurs without an applied gate-voltage,[14] and the n-doped effect is completely induced by the substrate. Fig.3(b) shows the precise K-resolved DOS around K of the carbon atom occupying the atop B site and Fig.3(c) shows that of the carbon atom occupying the other sublattice. Around the K point, the valence band and conduction band of the two sublattices do not touch each other due to the symmetry breaking of the two sublattices. They are different because of the rehybridization of the valence band and conduction band states at the same Dirac point, as illustrated in Fig. 3(d). For carbon over boron, the conduction bands degenerate while for carbon in the other sublattice, the valence bands degenerate. The separation between the conduction band peak of one carbon and the valence band peak of the other carbon at K is about 0.18 eV which is in good agreement with the value determined from calculated band structure. The Fermi level is above this gap due to substrate induced doping. The valence Dirac cone is populated with electrons which have nearly zero effective-mass and very high mobility.

Similar calculations and analysis were carried out for structure A1, and its electronic structure is nearly the same as that of A2. The only noticeable difference is the slightly small band gap, 0.15 eV, which is due to the different small difference in atomic structures.

This n-doped graphene on the BN/Cu(111) substrate can be very useful in realization of graphene-based electronic devices. It was demonstrated recently that p-type graphene can be easily realized experimentally by surface modification with electron acceptor molecule.[31] But a simple and effective method to fabricate p-n junction based on graphene is still lacking. Based on results of present study, it would be possible to massive produce p-n junctions by depositing electron acceptor molecules on certain regions of graphene eptaxially grown on BN/Cu(111) substrate. Furthermore, because the gap is just 0.5 eV below the Fermi-level, the Fermi-level can be easily shifted inside the gap by adsorption of molecule or applying a gate voltage to make graphene a real semiconductor. With a 0.2 eV band gap, graphene would behave like a narrow-gap semiconductor, such as PbTe or PbSe. It may be used as a material in infrared light emitting or detecting devices. One example would be light emitting quantum dots, which have much more advantages than conventional devices.

In conclusion, we have carried out a first principles investigation on graphene grown on Cu(111) surface with a h-BN buffer layer. Electrons transfer from the copper substrate to graphene through the BN buffer layer is predicted which results in a n-doped graphene in the absense of a gate voltage. A gap opening at the Dirac point just 0.5 eV below the Fermi-level is observed. The size of the gap (0.2 eV) is comparable to that of a typical narrow gap semiconductor. The Fermi-level can be easily shifted inside this gap to make graphene a semiconductor. Considering that the gap size of graphene on h-BN or clean Cu(111) is only a few meV,[20] it would be possible to engineering the gap of graphene through the tuning the interaction between the buffer layer and the metal surface by choicing different metal surface or buffer layer.

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TABLE I: Interlayer distances, as indicated in Fig. 1, of fully relaxed structures. All values are given in Å.

	d_0	d_1	d_2	d
A1	3.036	2.485	1.990	2.024
A2	3.044	2.499	1.991	2.022
Cu(111)			2.010	2.023

FIG. 1: The two most stable structures of graphene grown on Cu(111) with a h-BN buffer layer between them. A top view and a side view are presented in each case. The Cu atoms are represented using big grey spheres and their darkness increases with the distance from the surface. The carbon atoms are represented by small dark spheres. Nitrogen and boron atom are represented by medium sized blue and pink spheres respectively. d_0, d_1, d_2 and d represent interlayer spacings and their values are given in Table I.

FIG. 2: Band structure of (a) clean Cu(111); (b) h-BN on Cu(111); and (c) graphene on the BN/Cu(111). The Fermi level is indicated by dash line.

FIG. 3: (a) K-resolved DOS of the graphene layer. (b) K-resolved DOS of carbon atop B along the path indicated in (d). (c) Same as (b) but for carbon of the other sublattice. (d) Schematic diagram to show the band opening at Dirac point due to symmetry breaking between the two sublattice (A & B).